

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 122 324
B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 07.01.88

(21) Application number: 83111302.2

(22) Date of filing: 11.11.83

(51) Int. Cl.⁴: **C 07 C 103/87**, A 61 K 7/06,
A 61 K 7/48

(54) Polyquaternary ammonium compounds and cosmetic compositions containing them.

(30) Priority: 15.04.83 US 485197

(43) Date of publication of application:
24.10.84 Bulletin 84/43

(45) Publication of the grant of the patent:
07.01.88 Bulletin 88/01

(84) Designated Contracting States:
CH DE FR GB LI NL SE

(58) References cited:
GB-A-2 066 663

(73) Proprietor: MIRANOL INC.
68 Culver Road
Dayton New Jersey (US)

(72) Inventor: Desai, Bharat B.
5 Sebring Round
Belle Mead, NJ (US)

(74) Representative: Baillie, Iain Cameron et al
c/o Ladas & Parry Isartorplatz 5
D-8000 München 2 (DE)

EP 0 122 324 B1

The file contains technical information
submitted after the application was filed and
not included in this specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

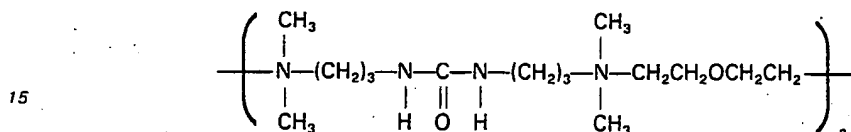
Courier Press, Leamington Spa, England.

Description

Background of the invention

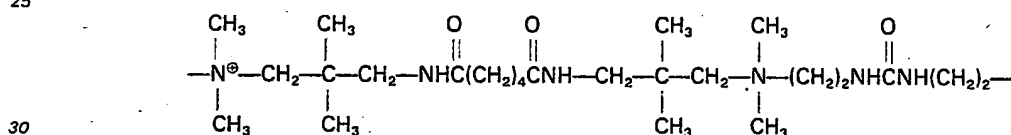
The invention relates to scale inhibitors, flocculants and conditioning agents for skin and hair, and processes for their preparation and their use. The compounds of this invention are novel polyquaternary ammonium compounds.

U.S. Patent No. 4,157,388 of Christiansen describes compositions containing polyquaternary ammonium compounds for use as hair conditioners and antistats and humectants for fibrous textile products. These compounds are generally liquid at room temperature. Mirapol® A-15 is a compound in accordance with Examples of Christiansen having the formula:



wherein n is at least one. The present polyquaternary ammonium compounds were found to be easier to work with since they do not generally require a particular order of addition and can be added in the oil or water phase. The present compounds in general also are found to have a better water solubility than the prior art compounds of Christiansen.

British Patent Specification GB-A-2066663 describes a variety of polyquaternary compounds and states that they are of use in cosmetics. A very wide range of materials is described. In Example 45 there is described a polymer containing a unit of the formula

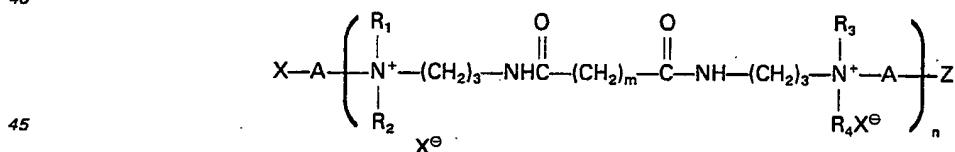


No cosmetic formulation using this compound was reported, however.

Summary of the invention and description of the preferred embodiments

The compounds of the present invention are conditioners and softeners having outstanding properties for use in hair and skin care compositions such as shampoos, soaps and lotions, and for use in scale inhibition and as flocculants.

The present compounds are of the general Formula (I):



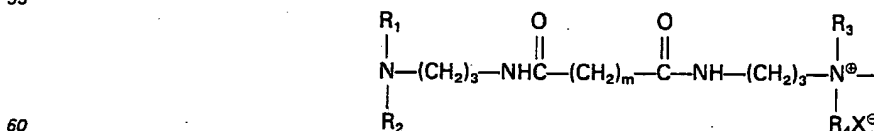
wherein R₁, R₂, R₃ and R₄ may be the same or different and are selected from the group consisting of hydrogen, methyl, ethyl, propyl, —CH₂CH₂OH, —CH₂CH(OH)CH₃ and —CH₂CH₂(OCH₂CH₂)_pOH wherein p is an integer from 0 to 6 with the proviso that not all of R₁, R₂, R₃ and R₄ are hydrogen;

n is at least one, and ranges up to 100 or more;

m is an integer from 4 to 34;

X is halogen;

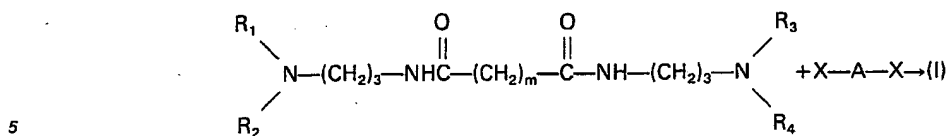
Z is halogen or amino-diamido ammonium residue of the formula



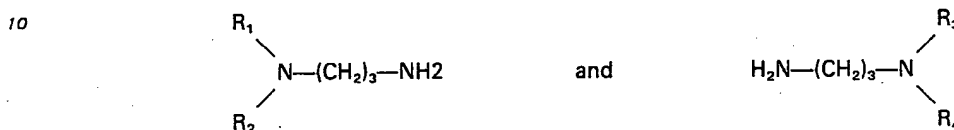
and

A is —CH₂CH₂OCH₂CH₂— or (CH₂)₆—.

The polyquaternary compounds are prepared by condensation of a polyamine and a quaternizing agent as follows:



The polyamine in turn is prepared by condensation of two diamino compounds with a dicarboxylic acid. The diamino compounds are of the formula



and may be identical, wherein R_1 and R_2 are identical to R_3 and R_4 .

The polyquaternary ammonium compounds of the invention are generally present in amounts of from about 1 to 10% by weight based on the total cosmetic composition. Shampoos and liquid soaps generally contain about 1 to 10% by weight and lotions generally contain about 0.5 to 5% by weight.

The cosmetic formulations comprise a suitable cosmetic carrier, the composition of which carrier depends on the purpose for which the final composition is intended. Thus, different carriers will be used dependent on whether the composition is to be used as a shampoo, a soap etc. These carriers are as described in the art. They may contain surfactants such as sodium lauryl sulfate, sodium lauryl ether sulfate, sodium lauryl sarcosinate, lauroamphocarboxyglycinate or co-coamphocarboxyglycinate, solvents such as glycol and propylene glycol, proteins, citric acid, coloring agents, preservatives, fragrances, mineral oils, thickeners such as sodium chloride, PEG 6000 distearate, PEG 80 sorbitan laurate, cocamide DEA, lauramide DEA or hydroxypropyl methylcellulose, vitamins, silicones, emollients such as lanolin, isopropyl palmitate, isopropyl myristate or petrolatum and viscosity builders such as carrageenan, carbomers or cocamidopropyl hydroxy sultaine. Where appropriate, CTFA designation is provided herein above and hereinafter.

Example I

A. To a reaction flask was charged 438 grams (3 moles) of adipic acid. After heating to about 55°C, 612 grams (6 moles) of dimethylamino-propylamine was added in about five minutes. During this addition the temperature rose to 101°C. The reaction mixture was heated to 165–170°C in about 3 to 4 hours. Distillation started at about 147°C. After a temperature of 165°C was reached, 62 grams of dimethylamino-propylamine (DMAPA) was added over a half hour period. The reaction mixture was then heated to 180 to 185°C in about two hours. After a temperature of 180°C was reached, 62 grams of DMAPA was added in about a half hour and the temperature maintained at 180–185°C for 1/2 hour. Vacuum was applied to remove water and excess DMAPA at a gradual increase to 5–10 mm. The vacuum of 5–10 mm was maintained for an hour at 180–185°C. The reaction mixture was cooled to 100°C and vacuum decreased to recover Adipic Condensate.

The above reaction was repeated by replacing adipic acid (1) with equal molar amounts of azelaic acid and (2) with equal molar amounts of dimer acid $HOOC-(CH_2)_{34}-COOH$.

B. To a two liter reaction flask was charged 282.73 grams (0.88 moles) of Adipic Condensate formed under Example A above and 152.24 g water and the mixture was heated to 90°C. Over four hours 122.28 g (0.855 moles) dichloroethylether was added while a temperature of 90–100°C was maintained. After the addition was completed, the reaction mass was heated to 100°C and held for 5 hours at about 100°C. The reaction was found to be 99.7% completed by chloride ion analysis.

115.8 g Water was added to the amber colored material and the mixture heated to distill 51.4 g distillate to remove traces of unreacted dichloroethylether. The final product was a clear amber colored liquid. The pH of a 10% aqueous solution was 8.32. The solids content was 68.2% by Karl Fischer (31.8% water) determination (as described by the American Oil Chemistry Society). The compound was found to have a value for n of about 115, determined from an intrinsic viscosity average molecular weight \bar{M}_w of 52,500 and an \bar{M}_n (number average molecular weight) of 45,800.

Example II

The above reaction B was repeated by replacing the Adipic Condensate by the product of Example A using azelaic acid rather than adipic acid resulting in an azelaic acid derived product of the invention for use in Conditioning Shampoo C hereafter.

Example III

The above reaction B was repeated by replacing dichloroethylether with 1,6-dichloro-hexane.

0 122 324

Example IV

Also, azelaic acid derivative was prepared by reacting azelaic condensate with 1,6-dichloro-hexane.

Application Examples

Two polyquaternaries according to the invention were evaluated as conditioners in hair and skin care products.

Four formulations were prepared having the following ingredients:

		Conditioning shampoo			
		A	B	C	D
10	Sodium lauryl ether sulfate	21.0	21.0	21.0	21.0
15	Mirataine® CB	15.0	15.0	15.0	15.0
	Miranol® C2M conc.	10.5	10.5	10.5	10.5
	Mirapol® A-15	2.1	—	—	—
20	Product of Example IB	—	2.1	—	—
	Product of Example II	—	—	2.1	—
25	Water	51.4	51.4	51.4	53.5

Each formulation was adjusted to a pH of 7.0.

Mirataine CB is cocamidopropyl betaine and is a high foamer and viscosity builder.

Miranol C2M conc. is a viscous clear aqueous amphoteric surfactant solution derived from coconut fatty acids, specifically a dicarboxymethylated derivative of cocoimidazoline.

Mirapol A-15 is a hair and skin conditioner as described in U.S. Patent No. 4,157,388.

The four formulations were evaluated by testing of hair swatches as to wet comb and dry comb results, antistatic effect, softness, shine etc. Formulations B and C were found to perform better than A as regards conditioning ability, that is manageability and wet and dry comb out. C was found to be slightly better than B.

		Conditioning shampoo			
		A	B	C	D
40	Alpha olefin sulfonate (A.O.S.) (40%)	15.0	15.0	15.0	15.0
	Miranol® 2MCAS-mod.	15.0	15.0	15.0	15.0
45	Mirataine® CBS	15.0	15.0	15.0	15.0
	Mirapol® A-15	2.1	—	—	—
	Example IB	—	2.1	—	—
50	Example II	—	—	2.1	—
	Polysorbate 20 (Tween® 20, ICI Americas Inc.)	2.0	2.0	2.0	2.0
55	Water	50.9	50.9	50.9	53.0

Miranol 2MCAS-mod. is a mixture of the lauryl sulfate and laureth—3 sulfate salts of a dicarboxymethylated derivative of a cocoimidazoline having one-eye irritating properties.

Mirataine CBS is cocamidopropyl hydroxysultaine.

Each formulation was adjusted to a pH of 7.0.

The same evaluation as above was performed on hair swatches and again C was found the best and B second best.

O 122 324

	Soft soap				
	A	B	C	D	E
5	A.O.S. (40%)	15.0	15.0	15.0	15.0
	Cedepal® TD 404M	10.0	10.0	10.0	10.0
	Mirataine® CB	20.0	20.0	20.0	20.0
10	Cocamide DEA (super amide GR, Onyx Chem. Co.)	2.5	2.5	2.5	2.5
	Mirapol® A-15	2.1	—	—	—
15	Example IB	—	2.1	—	—
	Example II	—	—	2.1	—
20	Polyquaternium 7 Merquat 550 (Merck Chem. Co.)	—	—	2.1	—
	Glycol stearate (Cerasynt, IP Van Dyk & Co.)	1.0	1.0	1.0	1.0
25	Glydant® (DMDM hydantoin, Glycochemicals)	0.2	0.2	0.2	0.2
	NaCl	1.0	1.0	1.0	1.0
30	Water	48.2	48.2	48.2	50.3

The pH of each formulation was adjusted to 7.0.

Cedepal TD 404 M is sodium trideceth sulfate.

Super Amide GR is a cocodiethanolamide.

35 Merquat 550 is a cationic polymer.

Glydant is a preservative.

A panel of five people after washing their hands with the five formulations chose C as the best in afterfeel and skin conditioning, B was the second best and slightly better than D.

40	Sheen activator				
	A	B	C	D	
	Water	81.4	81.4	81.4	83.5
45	Mirapol® A-15	2.1	—	—	—
	Example IB	—	2.1	—	—
	Example II	—	—	2.1	—
50	Glycerine	10.0	10.0	10.0	10.0
	Peptein® 2000 (Hormel)	5.0	5.0	5.0	5.0
55	Phenoxyethanol (Emeressence 1160, Emery Industries, Inc.)	1.0	1.0	1.0	1.0
	Cellosize® QP 4400 (Union Carbide)	0.5	0.5	0.5	0.5

60 The formulations were adjusted to a pH of 5.5.

The four formulations above were evaluated as sheen activators and pre-style lotions to determine enhancement in shine and setting properties.

A panel of five people chose C as the best and B as second best.

65

0 122 324

Skin moisturizer/conditioner

	A	B	C	D
5 Self emulsifying wax	7.5	7.5	7.5	7.5
PEG-400 Distearate	2.5	2.5	2.5	2.5
Stearic acid	1.0	1.0	1.0	1.0
10 Cetyl alcohol	1.0	1.0	1.0	1.0
Mirapol A-15	2.1	—	—	—
Example IB	—	2.1	—	—
15 Example II	—	—	2.1	—
Merquat 100	—	—	—	2.1
20 Propylene glycol	3.5	3.5	3.5	3.5
Methyl paraben	0.1	0.1	0.1	0.1
Propyl paraben	0.2	0.2	0.2	0.2
25 Water	82.1	82.1	82.1	82.1

Prototype C was chosen as the best in skin Softening and Conditioning. Prototype B was second best. The new polyquaternary ammonium compounds were evaluated as antistats in hair care products. Eight formulations were prepared having the following ingredients:

	A	B	C	D	E	F	G	H	Control (untreated)
35 Sodium lauryl ether sulfate (Maprofix ES)	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	—
Mirataine CB	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	—
40 Miranol C2M	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	—
Example IV*	1.5	—	—	—	—	—	—	—	—
45 Example II*	—	1.5	—	—	—	—	—	—	—
Example III*	—	—	1.5	—	—	—	—	—	—
Example IB*	—	—	—	1.7	—	—	—	—	—
50 Mirapol A-15*	—	—	—	—	1.5	—	—	—	—
Merquat 100*	—	—	—	—	—	2.5	—	—	—
55 Polymer JR-400* (3% solution)	—	—	—	—	—	—	33.3	—	—
Water	52.0	52.0	52.0	51.8	52.0	51.0	20.2	53.5	—
60 X10 ⁻⁷ Coulombs	9.0	10.2	9.7	1.4	7.2	7.1	8.4	9.2	4.7

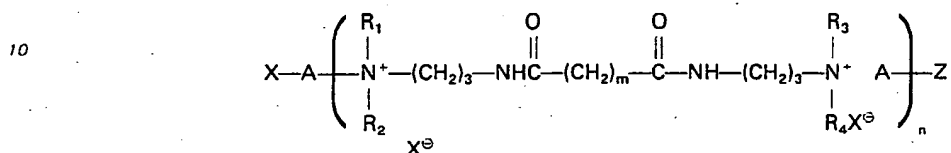
* Used 1% on active basis.

Hair swatches were soaked for half hour in a 25% solution of the above formulas and rinsed with 40°C water for one minute. The hair swatches were dried overnight at ambient temperature and the antistatic

property was evaluated by measuring electrostatic charges with an Electrometer (Keithley Model 610 C). Formulation (D) exhibited the lowest static charge of the eight formulas. There was no significant difference in values obtained for the other formulations.

5 Claims

1. Polyquaternary ammonium compounds of the formula:



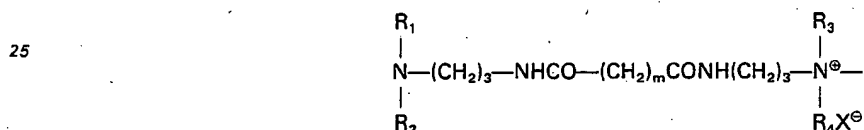
15 wherein R_1 , R_2 , R_3 and R_4 are the same or different and are selected from the group consisting of hydrogen, methyl, ethyl, propyl, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ and $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OH}$ wherein p is 0 or an integer from 1 to 6, with the proviso that not all of R_1 , R_2 , R_3 and R_4 are hydrogen;

n is at least one,

20 m is an integer from 4 to 34;

X is halogen;

Z is halogen or amino-diamido ammonium residue of the formula



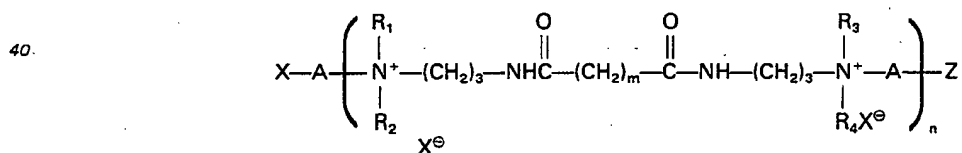
30 and

A is $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ or $(\text{CH}_2)_6-$ said compound having a weight average molecular weight of about 52,000.

2. Compound according to claim 1, wherein the ratio of the weight average molecular weight to the number average molecular weight is about 1.1.

35 3. A compound according to either of the preceding claims, wherein m is 4 or 7.

4. A cosmetic composition which comprises a suitable cosmetic carrier and a quaternary ammonium compound of the formula:



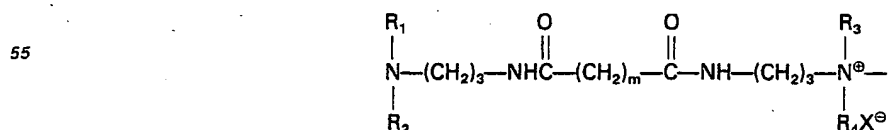
45 wherein R_1 , R_2 , R_3 and R_4 are the same or different and are selected from the group consisting of hydrogen, methyl, ethyl, propyl, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ and $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OH}$ wherein p is 0 or an integer from 1 to 6, with the proviso that not all of R_1 , R_2 , R_3 and R_4 are hydrogen;

n is at least one;

50 m is an integer from 4 to 34;

X is halogen;

Z is halogen or amino-diamido ammonium residue of the formula



60 and

A is $-\text{CH}_2\text{CH}_2-\text{OCH}_2\text{CH}_2-$ or $(\text{CH}_2)_6-$ wherein said quaternary compound has a weight average molecular weight of about 52,000.

5. A composition according to claim 4 wherein said quaternary compound has a ratio of weight average molecular weight to number average molecular weight of about 1:1.

65 6. A composition according to either of claims 4 and 5, wherein m is 4 or 7.

7. A composition according to any one of claims 4 to 6, wherein the cosmetic carrier is one for use in hair formulations.

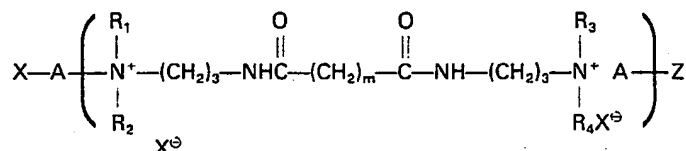
8. A composition according to claim 7, wherein the hair formulation is a shampoo.

9. A composition according to any one of claims 4 to 7, wherein the cosmetic carrier is one for use in skin care products.

10. A composition according to claim 9, wherein the skin care product is a soap.

Patentansprüche

1. Polyquaternäre Ammoniumverbindungen der Formel



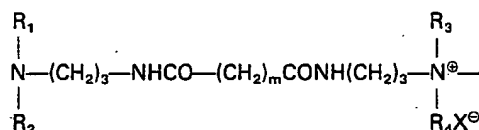
in welcher die Reste R_1 , R_2 , R_3 und R_4 gleich oder verschieden sind und aus der Gruppe von Wasserstoff, Methyl, Ethyl, Propyl, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ und $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OH}$ ausgewählt sind und in der p den Wert 0 oder den einer ganzen Zahl von 1 bis 6 hat, mit der Maßgabe, daß nicht alle Rest R_1 , R_2 , R_3 und R_4 Wasserstoff sind,

n mindestens eins ist,

m eine ganze Zahl von 4 bis 34 bedeutet,

X für ein Halogenatom steht,

Z ein Halogenatom oder einen Amino-diamido-ammoniumrest der Formel



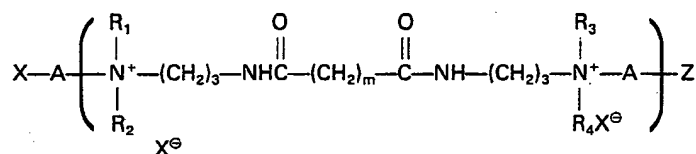
bedeutet, und

A für $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$ oder $(\text{CH}_2)_6-$ steht, wobei das gewichtete Durchschnittsmolekulargewicht etwa 52 000 beträgt.

2. Verbindung nach Anspruch 1, in der das Verhältnis aus gewichtetem Durchschnittsmolekulargewicht und numerischem Durchschnittsmolekulargewicht etwa 1.1 beträgt.

3. Verbindung nach einem der vorstehenden Ansprüche, in welcher m den Wert 4 oder 7 hat.

4. Kosmetische Zusammensetzung, welche einen geeigneten kosmetischen Träger und eine quaternäre Ammoniumverbindung der Formel



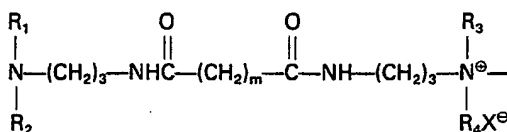
enthält, in der die Reste R_1 , R_2 , R_3 und R_4 gleich oder verschieden sind und aus der Gruppe von Wasserstoff, Methyl, Ethyl, Propyl, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ und $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OH}$ ausgewählt sind, und in der p den Wert 0 oder den einer ganzen Zahl von 1 bis 6 hat, mit der Maßgabe, daß nicht alle Reste R_1 , R_2 , R_3 und R_4 Wasserstoff sind,

n mindestens eins ist,

m eine ganze Zahl von 4 bis 34 bedeutet,

X für ein Halogenatom steht,

Z ein Halogenatom oder einen Amino-diamido-ammoniumrest der Formel



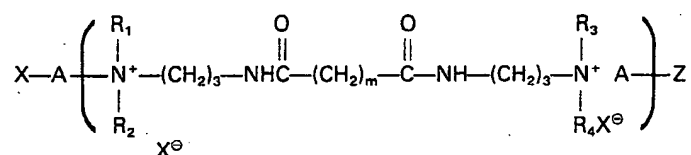
bedeutet, und

A für $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ oder $(\text{CH}_2)_6-$ steht, wobei die quaternäre Verbindung eingewichtetes Durchschnitts-Molekulargewicht von etwa 52 000 hat.

5. Zusammensetzung nach Anspruch 4, in der das Verhältnis aus gewichtetem Durchschnitts-Molekulargewicht und numerischem Durchschnitts-Molekulargewicht in der quaternären Ammoniumverbindung etwa 1.1 beträgt.
6. Zusammensetzung nach einem der Ansprüche 4 und 5, in der m den Wert 4 oder 7 hat.
7. Zusammensetzung nach jedem der Ansprüche 4 bis 6, in der der kosmetische Träger ein für Haar-Präparate gebräuchlicher Träger ist.
8. Zusammensetzung nach Anspruch 7, in der das Haarpräparat ein Shampoo ist.
9. Zusammensetzung nach jedem der Ansprüche 4 bis 7, in der der kosmetische Träger ein für Hauptpflegemittel gebräuchlicher Träger ist.
10. Zusammensetzung nach Anspruch 9, in der das Hauptpflegemittel eine Seife ist.

Revendications

1. Composés de poly(ammonium quaternaire) de formule:



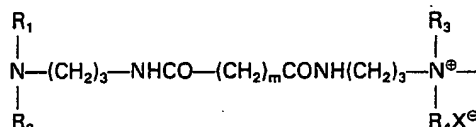
- dans laquelle R_1 , R_2 , R_3 et R_4 peuvent être identiques ou différents et sont choisis dans le groupe constitué par un hydrogène, un groupe méthyle, éthyle, propyle, $-\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ et $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OH}$, où p est un nombre entier de 0 à 6, à condition que R_1 , R_2 , R_3 et R_4 ne soient pas tous des atomes d'hydrogène;

n est au moins égal à 1;

m est un nombre entier de 4 à 34;

X est un halogène;

Z est un halogène ou un résidu amino-diamido-ammonium de formule

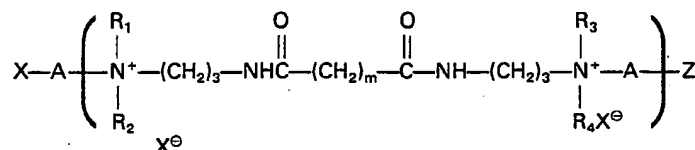


- et A est $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ ou $(\text{CH}_2)_6-$, ledit composé ayant un poids moléculaire moyen en poids d'environ 52 000.

2. Composé selon la revendication 1, dans lequel le rapport du poids moléculaire moyen en poids au poids moléculaire moyen en nombre est d'environ 1,1.

3. Composé selon l'une quelconque des revendications précédentes, dans lequel m est égal à 4 ou 7.

4. Composition cosmétique qui comprend un véhicule cosmétique convenable et un composé d'ammonium quaternaire de formule:



- dans laquelle R_1 , R_2 , R_3 et R_4 peuvent être identiques ou différents et sont choisis dans le groupe constitué par un hydrogène, un groupe méthyle, éthyle, propyle, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ et $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OH}$, où p est un nombre entier de 0 à 6, à condition que R_1 , R_2 , R_3 et R_4 ne soient pas tous des atomes d'hydrogène;

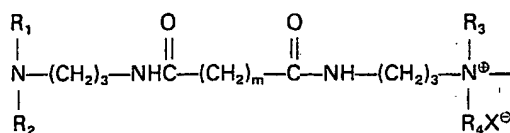
n est au moins égal à 1;

m est un nombre entier de 4 à 34;

X est un halogène;

Z est un halogène ou un résidu amino-diamido-ammonium de formule

0 122 324



5

et A est $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ ou $(\text{CH}_2)_6-$, dans laquelle ledit composé quaternaire a un poids moléculaire moyen en poids d'environ 52 000.

5. Composition selon la revendication 4 dans laquelle ledit composé quaternaire a un rapport du poids moléculaire moyen en poids au poids moléculaire moyen en nombre d'environ 1,1.

10 6. Composition selon l'une quelconque des revendications 4 et 5, dans laquelle m est égal à 4 ou 7.

7. Composition selon l'une quelconque des revendications 4 à 6, dans laquelle le véhicule cosmétique est un véhicule utilisable dans les formulations pour cheveux.

8. Composition selon la revendication 7, dans laquelle la formulation pour cheveux est un shampooing.

15 9. Composition selon l'une quelconque des revendications 4 à 7, dans laquelle le véhicule cosmétique est un véhicule utilisable dans les produits de soins de la peau.

10. Composition selon la revendication 9, dans laquelle le produit de soins de la peau est savon.

20

25

30

35

40

45

50

55

60

65